Filling and Fragmentation of a Single Pore of Catalyst Particle in Heterogeneous Catalytic Polymerizations

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Introduction

Essential principles of the growth of polyolefin particles from supported porous catalysts were discussed in a number of experimental and modeling studies, e.g., Kakugo et al (1989), Noristi et al (1994), Bonini et al (1995), Estenoz and Chiovetta (1996). Experimental studies resulted in a number of phenomenological concepts, such as fragmentation of the catalyst carrier, replication of its shape, multi-grain model etc. Characterizations of catalyst and polymer particle morphologies were based on microscopy images obtained by SEM, TEM and X-ray techniques as well as on mercury porosimetry and BET measurements. Proposed phenomenological concepts were successfully implemented mostly as reaction-transport models of growing particles, such as polymer flow, multi-grain or dusty fluid models, e.g., Galvan and Tirrell (1986), Hutchinson et al (1992) and Kosek et al (2001). These models were successfully applied, for example, to following problems: (i) the particle overheating phenomenon, (ii) the effect of intra-particle transport on the rate of polymerization and product properties, and (iii) the effects of sorption and transport of low molecular weight species in the polymer phase on particle growth.

The above-mentioned mathematical models typically introduce certain ad hoc effective spatial scales to the description of particle morphology and intra-particle transport processes and therefore we use the term "*effective-scale models*" or "*coarse-grained models*" to describe this principal feature. The quantitative characterization of particle morphology in these models is loose and the predictive capabilities in terms of the morphogenesis of polymer particles are limited. Our approach to the investigation of principal rules of particle morphogenesis is based on the meso-scopic characterization and representation of catalyst and polymer particles and we use the generic term "*meso-scopic models*" in this context.



Figure 1. (a) Sample of SEM image of catalyst particle and (b) corresponding 3D reconstructed porous particle.

Principal tools of the meso-scopic analysis and modeling

Characterization of porous structures and hetero-phase morphologies. Thousands of SEM and/or other microscopy images of catalyst and polyolefin particles are available in industrial and academic research laboratories, e.g., Debling and Ray (2001), Weickert et al (1999). The extraction of quantitative information from these images and systematic linking of this information to the catalyst particle architecture, reaction conditions and final particle morphology is required. The porous structure (or any general hetero-phase structure) can be represented by phase function, whose statistical properties could be described, for example, by porosity, two-point correlation function(s), probability density of the covering radius, or Minkowski functionals, cf. Adler and Thovert (1998). Powerful algorithms, such as thresholding of Gaussian and specifically correlated random fields, simulated annealing, or Poissonian generation of polydisperse spheres, could be employed to reconstruct spatially 3D porous structures possessing the same porosity and other selected characteristics as the original microscopy image of microtome sections, cf. Roberts and Teubner (1995), Sheehan and Torquato (2001), Thovert et al (2001).

Table 1. Effective transport properties of catalyst and polymer particles calculated from 3D reconstructed replicas of the pore structure, where ε is the porosity, $\sigma = D_{\text{eff}}/D$ is the ratio of effective and bulk diffusivity, σ_{inv} is analogically defined dimensionless conductivity of solid phase, *K* is the permeability and *L* is the pore space correlation length.

Sample	ε	σ	σ_{inv}	$K / 10^{-15} \text{ m}^2$	<i>L</i> / µm
1B1B	0.2495	0.0466	0.5676	9.73	2.1385
1AB	0.2913	0.0691	0.5042	17.0	2.1810
1B1A	0.3329	0.0942	0.4459	29.09	2.2235
2C	0.3928	0.1302	0.3479	2.21	0.5885
2CD	0.4350	0.1636	0.2944	2.50	0.5070
2D	0.4765	0.1981	0.2471	2.57	0.4252

Calculation of effective transport properties. The reconstructed spatially 3D replicas of the particle pore space allow us to calculate the effective transport and mechanical properties, such as effective diffusivity, heat conductivity, permeability or effective mechanical properties. Calculated effective transport properties could serve as inputs to effective scale models mentioned above. This research field is still open, particularly in the case of broad pore size distributions, cf. Mourzenko et al (2001). Hoel et al (1994) and Sliepcevich et al (2000) report actual measurements of transport properties of polymer particles.



Figure 2. Prediction of fractures in a thin section of catalyst particle computed by geometrical methods.

Analysis of catalyst support fragmentation by geometrical methods. The rigorous description of the fragmentation process should involve the simulation of pore filling by polymer, the calculation of stresses acting on the catalyst support and the simulation of the formation of fractures in the catalyst support. However, this approach is computationally demanding for realistically sized samples of catalyst support. developed computationally Therefore, we feasible geometrical method to approximate the fragmentation process. Our original algorithms, i.e., Delaunay tessellation generalized into space non-Euclidean with metrics and the

disconnection of the skeleton of the solid phase are described in detail in (Grof et al, 2002). The skeletonization algorithm is based on the conditional thinning and could be also employed to create network models of the pore phase, which are popular, e.g., for the interpretation of mercury porosimetry data (Liang et al, 2000).

Force interactions in agglomerates of spherical micro-elements. The porous structure of catalyst/polymer particles could be alternatively represented by the agglomerate of spherical micro-elements. Such micro-elements could be either of one type, e.g., micro-grains constituting the basic building blocks of the multi-grain morphology, or of two types, i.e. micro-elements representing the semi-continuos catalyst and polymer phases in the early stages of particle growth. Considered micro-elements are subjected to visco-elastic interactions with neighboring micro-elements and/or with external forces. Such models are capable to qualitatively predict, e.g., the formation of hollow particles, formation of large cracks in polymer particles or replication of the particle shape (Grof et al, 2001). Similar phenomena were attempted to obtains by the effective-scale model employing the build up and relaxation of elastic tensions inside growing particles (Kittilsen et al, 2001).

Description of the investigated problem

This contribution continues in the development and validation of tools of meso-scopic modeling. A single pore of catalyst support is considered. A hybrid model considering simultaneously continuos and discrete representation of the problem simulates the filling of a single pore by polymer. The discrete part of the model is formed by the agglomerate of micro-elements. Hence this model describes not only the reaction, the transport through fluid and polymer phases and sorption processes, but also the visco-elastic flow of polymer and the force exerted by polymer on solid walls of catalyst carriers. The consequences of these simulations for pore clogging, fragmentation of catalyst carries and kinetic rate profiles of supported catalysts are systematically discussed and studied parametrically.



Figure 3. The scheme of a considered single pore of catalyst.

The binary and ternary force interactions among the catalyst and polymer micro-elements, movements of micro-elements, formation of new connections and breakage of stretched bonds between elements are taken into account in order to describe the morphological evolution of the system. The temperature dependence of visco-elastic properties of polymer material is also considered.

Conclusions

The above described tools of meso-scopic modeling enable us to systematically characterize porous and hetero-phase morphologies of catalyst/polymer particles at various stages of their development. Moreover, first-principle based modeling of particle morphogenesis and of related subjects is an excellent tool for deeper understanding and systematic organization of a large number of experimental data and empirical knowledge accumulated in this field. However, the validation of models requires strong interaction with experimental databases (including data from industrial reactors). For example, Furtek (1987) reports that characteristics of the pore phase of supported catalysts are affecting the yield and the composition of a copolymer.

Results of this study shall improve our understanding of the early stages of particle growth at the meso-scale level, particularly the problems of pore clogging and induction periods seen on kinetic rate profiles of certain catalysts (Steinmetz et al, 1997). Our results are also compared with experimental characterizations of the initial morphology of MgCl₂ and SiO₂-supported catalysts, e.g., Ferrero et al (1992), McDaniel (1981) and Niegisch et al (1992). We also compare the pore clogging and fragmentation of several hypothetical catalyst carriers possessing the regular structure.

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